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Determination of a Range of Concern for Mobile Source Emissions of Methanol

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Technical Report

Determination of a Range of Concern for Mobile Source Emissions of Methanol

by

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July, 1983

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16. ABSTRACT

This paper describes an effort by the Emission Control Technology Division of the Environmental Protection Agency (EPA) to suggest a range of concern for methanol (CH_3OH) emissions from mobile sources. In accordance with section 202 (a) (4) of the Clean Air Act (CAA) and due to a concern within industry as to what emission levels will be used as the basis for the evaluation of current and future technologies, a methodology was developed in order to bracket a range of concern for various unregulated pollutants. This paper uses the results frome two EPA contracts to apply this methodology specifically for an evaluation of methanol. Mathematical models previously designed for various exposure scenarios (such as enclosed spaces, expressways, and street canyons) were used to calculate the ambient air concentrations resulting from a range of potential mobile source methanol emissions. It was assumed that methanol fueled vehicles would have to meet the same exhaust emission standards as gasoline fueled vehicles currently meet. In conjunction with this work, a health effects literature search for methanol was conducted by Midwest Research Institute under contract to EPA to aid in the determination of the suggested range of concern. The results of the Midwest analysis suggest a range of concern for ambient methanol concentrations of from 4.5 mg/m^3 to 260 mg/m^3. It must be mentioned that the range of concern for methanol suggested in this report is based on its toxicological

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properties and not its photochemical reactivity nor any possible carcinogenic effects. The consideration of the photochemical reactivity and oxidant formation due to methanol is an important one but beyond the scope of this report. Furthermore, potential combined effects of exposure to other pollutants along with methanol have not been considered here.

Summary

This paper describes an effort by the Emission Control Technology Division of the EPA to suggest a range of concern* for methanol (CH_3OH) emissions from mobile sources. In light of the action called for in section 202(a)(4) of the Clean Air Act (CAA) (1)** and due to a concern within industry as to what emission levels will be used as the basis for the evaluation of current and future technologies, a methodology was developed in order to bracket a range of concern for various unregulated pollutants (2). This paper uses the results from two EPA contracts to apply this methodology specifically for an evaluation of methanol.

Mathematical models previously designed for various exposure scenarios (such as enclosed spaces, expressways, and street canyons) were used to calculate the ambient air concentrations resulting from a range of potential mobile source methanol emissions. It was assumed that methanol

*Range of concern is defined as a range of ambient concentrations (or corresponding vehicle emissions) of a given pollutant, the upper limit of which is the value above which the studies show that the pollutant causes so great a health risk as to strongly suggest it be avoided; the lower value of the range will be the lowest level at which there is some suggestion of adverse physiological effects.

**Numbers in parentheses denote references listed at end of report.

fueled vehicles would have to meet the same HC, CO, and NOx emission standards as gasoline fueled vehicles currently meet. In order to get a worst case estimate it was also assumed that the entire vehicle fleet would be methanol fueled with up to 25% having severe malfunctions.

In conjunction with this work, a health effects literature search for methanol was conducted by Midwest Research Institute under contract to EPA to aid in the determination of the suggested range of concern (3). The health effects associated with exposure to methanol ranged from weakness, shallow breathing and rapid pulse, to headaches, nausea, vertigo, vision defects, convulsions, and death, depending on exposure and individual susceptibility.

The results of the Midwest analysis suggest a range of concern for ambient methanol concentrations of from 4.5 mg/m^3 to 260 mg/m^3.* This corresponds to motor vehicle emission levels of from 1.58-91 g/mile to 107.1-6190.5 g/mile depending on the type of scenario chosen to represent public exposure. If the entire vehicle fleet were to run on methanol fuel, the estimated fleet emission factors are below the ranges of concern for all expressway and street canyon scenarios, as well as the typical tunnel scenario. In the

*1 mg/m^3 = 0.764 ppm.

severe roadway tunnel scenario, if 25% of the vehicles are assumed to be malfunctioning severely (e.g., non-functional catalyst), the resulting methanol concentration could be somewhat higher than the lower limit of the range of concern.

Parking garages are also estimated to remain below the range of concern, but personal garages could have methanol concentrations within the range of concern for brief periods of time due to vehicle warm-up exhaust emissions or hot soak evaporative emissions. Exposure resulting from potential self service methanol refueling (50 mg/m^3) is expected to be within the range but not above it.

It must be mentioned that the range of concern for methanol suggested in this report is based on its toxicological properties and not its photochemical reactivity nor any possible carcinogenic effects. The consideration of the photochemical reactivity and oxidant formation due to methanol is an important one but beyond the scope of this report. Furthermore, potential combined effects of exposure to other pollutants along with methanol have not been considered here.

I. Introduction

Changing technology (including different vehicle powerplants, fuels, and emission control systems) can significantly change the emissions from automobiles. This report deals with methanol emissions because of the possible use of methanol as an automotive fuel. The Clean Air Act requires EPA to evaluate the health risks of new vehicle technologies.

Methanol in vehicle exhaust results from incomplete combustion of methanol fuel in the engine, in the exhaust system, or in the catalytic converter. Other sources of methanol from vehicles are evaporative methanol emissions and refueling emissions.

Due to its toxic properties and the potential increased use of methanol as an automotive fuel, tests have been conducted to characterize methanol emissions as a function of driving cycle, engine type, and emission control system. These test results along with health effects test data determine whether methanol emissions from mobile sources could be of concern with respect to health and welfare.

To establish a range of concern for exposure to methanol via inhalation, Midwest Research Institute (MRI) compiled

information on its health effects in different exposure situations (3). That work forms the basis for the vehicle emissions range of concern suggested in this report.

II. General Information on Methanol

Methanol is a colorless flammable liquid with a lower heating value (heat content) half that of gasoline and a vapor pressure (volatility) about one third to one half that of gasoline. It burns in air with a transparent blue flame producing mostly H_2O and CO_2.

Methanol is used in industry as a solvent, a denaturant for ethanol, a dehydrator for natural gas, and as a raw material in the production of formaldehyde, methacrylates, methylamines, methyl halides, ethylene glycol, and plastics.

Methanol is a well-known poison, discussed today in most standard reference works on toxic chemicals. In the past, methanol's toxicity was debated, and, as late as 1936, doubts existed as to the toxicity of pure methanol. The toxicity of wood alcohol was attributed to its impurities by some authorities (4). A 1904 report by Wood and Buller documented the earliest recorded cases of methanol poisoning; it stated that 275 cases of blindness or death attributable to wood alcohol were reported between 1856 (when the first scientific report of toxicity was made) and 1904 (5). Nevertheless, methanol was a frequent component of liniments, toilet articles, perfumes, and some patent medicines well into this century.

Even today, exposure to small amounts of methanol occurs from a wide variety of sources. For instance, cigarettes have been found to contain 100 - 200 ug methanol/cigarette (6), and certain vegetables such as Brussels sprouts, celery, onions, parsnips, potatoes, and rutabaga have been reported to contain "large" or "very large" levels (unquantified) of methanol after boiling for 30 minutes (7). Occupational exposures to methanol are certainly possible in those industrial uses mentioned above, but the data available on this are very limited.

Alcoholic beverages which contain ethanol and which may be contaminated with methanol may also contribute to an individual's exposure to methanol and accumulation of methanol in the blood. Levels of 3.9 to 105.5 mg methanol/liter have been reported in commercial alcoholic beverages (8,9,10).

Alcoholics with high blood ethanol levels (100 mg/100 ml) tend to accumulate methanol in their blood at levels up to 2.7 mg/100 ml after an eleven day intoxication (9). Some of the methanol accumulated by alcoholics is believed to be derived from endogenous (originating within the body) sources and accumulated due to ethanol's disruption of methanol oxidation and elimination. That some methanol is endogenously produced is supported by studies finding

methanol levels of 0.06 to 0.49 mg/m^3 and 0.40 to 4.52 mg/m^3 (0.3 to 3.4 ppm) in normal human breath(11,12). Another study of 54 healthy nonsmoking adults found only 3.6% of 387 breath samples to contain methanol; the mean concentration when found was 0.549 mg/m^3(13).

In the section of this report concerning ambient concentrations, potential exposures from motor vehicles are given which can be compared to the exposures mentioned above.

III. Legislative Background

The Clean Air Act amendments of August 1977 included sections 202(a)(4) and 206(a)(3) which deal with mobile source emissions of hazardous pollutants from vehicles manufactured after 1978. These sections are as stated below:

202 (a)(4)

"(A) Effective with respect to vehicles and engines manufactured after model year 1978, no emission control device, system or element of design shall be used in a new motor vehicle or new motor vehicle engine for purposes of complying with standards prescribed under this subsection if such device, system, or element of design will cause or contribute to an unreasonable risk to public health, welfare, or safety in its operation or function.

(B) In determining whether an unreasonable risk exists under subparagraph (A), the Administrator shall consider, among other factors, (i) whether and to what extent the use of any device, system, or element of design causes, increases, reduces, or eliminates emissions of any unregulated pollutants; (ii) available methods for reducing or eliminating any risk to public health,

welfare, or safety which may be associated with the use of such devices, systems, or elements of design which may be used to conform to standards prescribed under this subsection without causing or contributing to such unreasonable risk. The Administrator shall include in the consideration required by this paragraph all relevant information developed pursuant to section 214."

206 (a)(3)

"(3) (A) A certificate of conformity may be issued under this section only if the Administrator determines that the manufacturer (or in the case of a vehicle or engine for import, any person) has established to the satisfaction of the Administrator that any emission control device system, or element of design installed on, or incorporated in, such vehicle or engine conforms to applicable requirements of section 202(a)(4).

(B) The Administrator may conduct such tests and may require the manufacturer (or any such person) to conduct such tests and provide such information as is necessary to carry out subparagraph (A) of this paragraph. Such requirements shall include a requirement for prompt reporting of the emission of any unregulated pollutant from a system, device or element of design if such

pollutant was not emitted, or was emitted in significantly lesser amounts, from the vehicle or engine without the use of the system, device, or element of design."

Prior to these amendments, EPA's guidance to the manufacturers regarding hazardous unregulated pollutants was contained in the Code of Federal Regulations, Title 40, section 86.078-5b. This subsection is stated as follows:

(1) "Any system installed on or incorporated in a new motor vehicle (or new motor vehicle engine) to enable such vehicle (or engine) to conform to standards imposed by this subpart:

(i) Shall not in its operation or function cause the emissions into the ambient air of any noxious or toxic substance that would not be emitted in the operation of such vehicle (or engine) without such system, except as specifically permitted by regulation; and

(ii) Shall not in its operation, function, or malfunction result in any unsafe condition endangering the motor vehicle, its occupants, or persons, or property in close proximity to the vehicle.

(2) Every manufacturer of new motor vehicles (or new motor vehicle engines) subject to any of the standards imposed by this subpart shall, prior to taking any of the action specified in section 203 (a)(1) of the Act, test or cause to be tested motor vehicles (or motor vehicle engines) in accordance with good engineering practice to ascertain that such test vehicles (or test engines) will meet the requirements of this section for the useful life of the vehicle (or engine)."

Before certification can be granted for new motor vehicles, manufacturers are required to submit a statement, as well as data (if requested by the Administrator), which will ascertain that the technology for which certification is requested complies with the standards set forth in section 86.078-5b. This statement is made in section 86.078-23(d).

The EPA issued an Advisory Circular (AC 76) in June 1978, to aid the manufacturers in complying with section 202 (a)(4). Manufacturers were asked to continue providing statements showing that their technologies did comply with the vehicle emission standards and also will not contribute to an unreasonable risk to public health and safety.

Another Advisory Circular (AC 76-1) was issued in November of 1978 continuing these procedures for 1980 and later model years. At that time, EPA began work to develop and implement a methodology which would provide a preliminary assessment of potential mobile source unregulated pollutant hazards in order to assist the manufacturers in deciding which, if any, unregulated pollutants are of particular concern.

Up to this time, several preliminary assessments have been made covering sulfuric acid, hydrogen cyanide and ammonia. In each of these cases, the preliminary assessment found no reason for suspecting a public health problem from the current fleet emissions of these pollutants, and recommended that further monitoring may be appropriate to be sure that new vehicle/emission control system configurations did not result in greatly increased emissions.

IV. Methodology Overview

Along with the previously mentioned activities, EPA, with the input from several interested parties, has developed a methodology for implementing section 202 (a)(4) of the CAA. This approach is explained in detail in EPA report number EPA/AA/CTAB/PA/81-2, "An Approach for Determining Levels of Concern for Unregulated Toxic Compounds from Mobile Sources" (2). Only a brief summary of this methodology will be presented in this report.

Under contract to EPA, Southwest Research Institute (SwRI), and Midwest Research Institute (MRI), have provided valuable information for this effort. SwRI developed or modified mathematical models for predicting ambient concentrations of mobile source pollutants for exposure situations including enclosed spaces, street canyons, and expressways. Once vehicle emissions for various vehicle categories have been determined for a particular pollutant, these models are used to calculate ambient concentrations for both severe and typical exposure situations for each scenario.

Health effects literature searches have been conducted by MRI to aid EPA in suggesting a range of concern for various selected pollutants. The upper level of the range is that value above which the studies show that the pollutant causes

so great a health risk as to strongly suggest it be avoided. The lower value of the range will be the lowest level at which there is some suggestion of adverse physiological effects. The region between these limits will be termed the "ambient air range of concern", indicating the bounds of uncertainty regarding evidence of adverse physiological effects caused by exposure to various concentrations of the pollutant. Any technology whose emissions result in ambient air concentrations within the range of concern should be subject to closer scrutiny. Technologies with emission levels above the highest value of the range should be considered "high risk" with respect to human health.

For the purpose of this report, this particular methodology has been used to develop a suggested range of concern specifically for motor vehicle emissions of methanol.

V. Vehicle Emissions of Methanol

This report considers only vehicles using 100% methanol fuel. Nationwide methanol emissions from motor vehicles are currently negligible due to the small number of methanol fueled vehicles, but the technology does exist to increase this use of methanol. Therefore, the following discussion examines the hypothetical scenario in which all vehicles are methanol fueled, as well as an intermediate scenario having 25% of the fleet methanol fueled.

The data in Table 1 are based on the assumption that methanol fueled vehicles will have to meet the same emission standards that gasoline fueled vehicles now meet, in order to be certified for sale. It is further assumed that on the average, in-use vehicles will exactly meet the HC standard, except those with malfunctions. The hydrocarbon (HC) standard (e.g. 0.41 g/mi for light duty vehicles on the FTP) would presumably apply only to the HC portion of any unburned alcohol in the exhaust or evaporative emissions. Since HC comprises only 50% of the mass of methanol, the standard to be met for actual methanol emissions would in effect be double that for gasoline (e.g. 0.82 g/mi for light duty vehicles on the FTP).

In order to better characterize methanol emissions and exposures under certain potential high concentration conditions, a few scenarios are considered which differ considerably from standard FTP conditions. For instance, the Hot Start FTP column in Table 1 was derived by taking the ratio of Hot FTP emissions to regular FTP emissions from actual methanol vehicle tests (23,25), and then multiplying that ratio by the emission standard for the FTP. This was also done for the highway (HFET) column. This was done to provide a more realistic emissions estimate for scenarios such as tunnels or highways where cold start emissions would not normally be encountered.

Table 1

Vehicle Emissions[a]
100% Methanol-Fueled Fleet
g/mile

Scenario (Driving Cycle Used)	Light Duty		Heavy Duty[b]		Weighted Average[c]	
	Normal	With 25% Malfunction	Normal	With 25% Malfunction	Normal	With 25% Malfunction
Street Canyon [d] (FTP)	1.17	2.60	5.47	11.03	1.44	3.12
Roadway Tunnel (Hot FTP)	0.08	1.22	4.05	8.94	0.33	1.70
Expressway (HFET) (7-Mode S.S.)	0.02	0.19	2.88	3.81	0.20	0.41
Personal & Parking Garages (Idle)	0.007[e]	0.24[e]	[f]	[f]	0.007[e]	0.24[e]

[a]Based on expected compliance with light-duty FTP hydrocarbon standard of 0.41 g/mile (0.82 g methanol/mi) and heavy-duty HC standard of 1.3 g HC/BHP-hr.

[b]g/KW-hr engine data converted to g/mile assuming 3 miles/gal methanol, 0.708 kg fuel/kW-hr.

[c]93.8% light-duty, 6.2% heavy-duty vehicle miles traveled.

[d]Includes evap emissions @ 0.35 g/mi for light-duty and 0.54 g/mi for heavy-duty, based on 1985 evap standards (2.0 LD, 3.0/4.0 HD HC g/test).

[e]g/minute results from one vehicle; 0.007 is with a warmed up engine and catalyst; 0.24 is with a warmed up engine and no catalyst.

[f]Not applicable to scenarios studied.

Light Duty Vehicles - Urban Emissions (FTP)

For the street canyon scenario, the FTP was chosen as the most representative driving cycle of those available. The first column of Table 1 shows the expected methanol exhaust emissions (0.82 g/mi) based on an HC standard of 0.41 g/mile, multiplied by 2 to account for the oxygen content of methanol. Recent tests on properly functioning 4-cylinder vehicles with oxidation and/or 3-way catalysts yielded methanol emissions less than this value. For instance, Ford Pintos with different degrees of engine modifications emitted between 0.3 and 0.6 g/mile (22), and a recent EPA test program using a methanol-fueled VW Rabbit and Ford Escort yielded emissions of 0.1-0.5 g/mile (15).

Hot Start "FTP"

For the severe case tunnel scenario, the average speed is 25 mph, so of the data available, the FTP was again chosen as the most representative driving cycle. However, in a tunnel, vehicles are assumed to be warmed up already so the hot start portion of the FTP data were used (Bags 2 and 3). The data collected for this show the hot start methanol emissions to be approximately 10% of the corresponding FTP emissions, not including the evaporative emissions, since they would not be a factor in emissions while actually driving. Using this proportion together with the effective FTP standard of 0.82

g/mile, the expected methanol exhaust emissions from the hot start portion of the FTP would be 0.08 g/mile.

Highway Emissions (HFET)

The EPA driving cycle chosen to represent the expressway scenario is the Highway Fuel Economy Test (HFET) with its average speed of 48.2 mph. Recent data (23, 25) from methanol fueled vehicles with 3-way catalysts and oxidation catalysts (VW, 3-way catalyst prototypes) show the HFET methanol exhaust emissions to be about 98% lower than the methanol emissions from the FTP. Applying this percent reduction to the FTP standard yields expected emissions of 0.02 g/mile for highway driving conditions. As with the hot start FTP calculations for the tunnel scenario, the expressway scenario does not include evaporative emissions.

Two contributing reasons for this large difference between FTP and HFET emissions could be differences in engine speed and differences in the thermal condition of the catalyst. The FTP includes a cold start with a large fraction of the overall emissions being emitted in the first part of the test before the catalyst is warmed up, but in the highway test, the catalyst is already warmed up. Some supporting evidence for the engine speed effect is found in two studies (17,25) using steady state tests. The first of these showed 95% lower methanol emissions at 3000 rpm than at 1000 rpm and the

second one showed a 25% - 65% decrease in methanol emissions at 50 mph relative to 30 mph. The actual engine speed in the HFET is a function of the vehicle transmission and axle gear ratios which may vary.

Heavy Duty Engines

As with light duty vehicles, heavy duty engines need to meet certain EPA criteria. The regulations call for no more than 1.3 g hydrocarbons per BHP-hr beginning with the 1985 model year. This, again, would probably apply only to the HC portion of any unburned fuel, so the effective limit for methanol exhaust emissions would be 2.6 g/BHP-hr.

For comparison, testing of a M.A.N. methanol-fueled heavy duty engine with an oxidation catalyst yielded methanol exhaust emissions of 0.4 g/BHP-hr (0.5g/kW-hr) on the 7 mode test and 0.7 g/BHP-hr (0.9 g/kW-hr) on the transient test procedure. Another engine, made by Volvo, used injection of a pilot charge of diesel fuel to ignite the methanol charge. When tested with an oxidation catalyst, the unburned methanol emissions were 0.67 - 0.75 g/BHP-hr (0.9 - 1.0 g/kW-hr). Without a catalyst these emissions increased to 1.6 - 3.7 g/BHP-hr (2.2 - 4.9 g/KW-hr) on the 7 - mode and transient tests, respectively.

To put these power-specific emissions into terms of g/mile, they can first be converted to g/kg fuel by dividing by the fuel consumption (kg fuel/kW-hr). Then, using fuel economy data from other heavy duty diesel tests (29) ranging from 44 - 69 liters/100 km, and adjusting for the different energy content of methanol vs. diesel fuel, a corresponding range of methanol emission factors on a per-mile basis can be calculated. This is how the heavy duty engine emission estimates shown in Table I were derived.

Evaporative Emissions

Emissions of evaporated fuel from methanol vehicles can contribute significantly to the overall vehicle methanol emissions. Therefore these emissions are included, where appropriate, in the fleet average emissions in Table I. These numbers include both diurnal heat build and hot soak evaporative emissions as specified in the Federal Register test procedure.

As was done with the FTP emissions above, we will assume that the evaporative gasoline standards would apply to the HC portion of evaporative emissions from methanol fueled vehicles. This would result in maximum methanol evaporative emissions of 4.0 g/test for light duty vehicles and 6.0 or

8.0 g/test for heavy duty engines and vehicles, depending upon their Gross Vehicle Weight Rating (GVWR).

These values can be converted into grams/mile for any scenario that would include evaporative emissions - namely street canyons. This is done by taking the total evaporative emissions per day (diurnal plus hot-soak) and then dividing by the miles driven per day. According to MOBILE2, in urban areas, the average light duty vehicle makes 3.05 trips/day, totalling 31.1 miles. Therefore, to estimate the equivalent g/mile emissions of a car meeting a 4.0 g/test methanol evaporative standard, it is necessary to know how much of the 4.0 grams is hot soak vs. heat build.

The hot soak test emissions are usually greater than the heat build emissions. For example, in-house tests of a fuel-injected methanol fueled VW Rabbit have shown hot soak test emissions to be approximately 1.3 times greater than heat build emissions (25). In similar tests at the University of Santa Clara, the ratio was about 3.0 (28). A couple of carbureted cars (1980 Ford Pintos modified to run on methanol) have also been tested. For these vehicles the ratio of hot soak to heat build emissions were greater, averaging 10.0.

From this rather limited data it appears that a reasonable rough estimate of the ratio of hot soak (HS) to heat build

(HB) emissions for methanol fueled vehicles would be 5.0.* From this, the grams methanol/mile can be calculated, based on a vehicle just meeting a 2.0 g/test evaporative HC standard.

(1) HS + HB = 4.0 grams methanol

(2) HS = 5 x HB

HB = 0.67 grams methanol

HS = 3.33 grams methanol

With one heat build/day, 3.05 hot soaks/day, and 31.1 miles/day, this results in 0.35 g methanol/mile.

Of the cars that have been tested so far, only one has exceeded these estimates - a carbureted 1980 Ford Pinto (designed to meet the California 2 g/test HC standard) with a total of 5.7 g/test. The other test vehicles (VW Rabbit, Ford Pinto, and Ford Escort) have ranged from 1.2 - 2.4 g/test by FID measurement uncorrected for methanol response,

*The corresponding ratio for gasoline fueled vehicles, per MOBILE2, is 0.59. It is not certain why there should be that much difference between methanol and gasoline, but it could possibly be related to the much greater heat of vaporization of methanol necessitating greater temperature for a given rate of evaporation. The FTP before the hot soak may result in a higher temperature or rate of vaporization compared to the heat build.

evaporative methanol emissions are estimated to be 0.54 g/mile.

Malfunction Conditions

A certain percentage of in-use vehicles have been found to operate in a less-than-optimum condition (34). For instance, a disconnected air injection system or a catalyst that has been either removed or poisoned with use of improper fuel will all increase emissions. The resulting emissions depend on the type and degree of malfunction, but at this time the most data are available for a severe malfunction. This would be the lack of a catalyst as compared to the presence of a working catalyst, including particularly the case of a catalyst equipped vehicle tested without a catalyst. Such a comparison shows the "malfunctioning" (no catalyst) vehicle methanol emissions to be much greater than catalyst equipped vehicles (references: no cat. 14 through 21,25; catalyst 15, 18 through 23,26,27,28). Table II gives the ratios used in computing the malfunction values in Table I. These are based on test data from one or more vehicles/engines.

which would be about 1.6 - 3.2 g/test if a typical methanol response factor of 0.75 is assumed.

Heavy Duty Evaporative Emissions

As mentioned above, the heavy duty vehicle evaporative emission standards beginning in model year 1985 (depending on GVWR) are 3.0 and 4.0 g HC/test, which corresponds to 6.0/8.0 g methanol/test. Per Mobile 2, the hot soak portion of the test contributes 37% of the total test emissions for 1984 and later model years, which methanol fueled vehicles would be. This fraction is based on gasoline data since no methanol fueled heavy duty evaporative data are available. Going through the calculation to determine g/mile, as was done with light duty vehicles, but using 6.88 trips/day and 36.70 miles/day for heavy duty vehicles yields 0.53 g/mile up to 14,000 GVWR and 0.70 g/mile methanol over 14,000 GVWR.

For purposes of computing an average heavy duty evaporative emission rate, the above two numbers need to be weighted according to their respective fractions of urban VMT. Using data from the MVMA (33), only 5% of the non-highway urban truck VMT is from combination trucks. This should serve as a good approximation of the truck VMT fraction over 14000 GVWR. Therefore, the weighted average heavy duty vehicle

Table II

Ratios of Malfunction (no catalyst)
to Non-Malfunction Exhaust
Methanol Emissions

	FTP	Hot FTP	HFET (HD 13-mode)	Idle
Light Duty	8.0	58.0	35.0	34.3
Heavy Duty	5.5	5.8	2.3	Not used

The potential effect of these malfunctions on ambient air concentrations of methanol is shown in columns 2 and 4 of Table III with 25% of the vehicles assumed to be malfunctioning. The 25% malfunction fraction was arrived at from FOSD* data indicating that in areas without Inspection/Maintenance, after 50,000 miles, 25% of the vehicles had at least one of the three malfunctions described above.

*FOSD: EPA Office of Mobile Sources Field Operations and Support Division.

VI. Methanol Ambient Air Concentrations

The methanol emission factor information provided in Table I can be used, in conjunction with the modeling techniques developed by Southwest Research Institute (2,33), to calculate the ambient air concentrations produced. Future work may identify other scenarios which would also be appropriate for the assessment of human exposure to exhaust pollutants, but, for this task, five exposure scenarios were investigated: roadway tunnels, street canyons, personal garages, parking garages and urban expressways. Two case situations, "typical" and "severe", were developed for each of the first four scenarios, and three cases were considered for the expressway scenario. Each situation has been considered separately; no cumulative effects have been determined at this point for these or other exposures to methanol. Reference (2) discusses the reasoning behind using these specific scenarios as well as the information used in the determination of the modeling techniques.

Table III presents ambient air concentrations of methanol calculated from the vehicle emissions listed in Table I for seven ambient situations. Evaluations of the garage situations are based on idle emission data from only one vehicle and evaporative emissions from five vehicles.

Two specific tunnel designs were chosen to estimate the two roadway tunnel cases. A newly designed, two lane roadway tunnel, with moderate traffic flow, is used for the typical condition, while an old design, heavily-traveled roadway tunnel is used for the severe condition (2). The calculations for the typical tunnel exposure situation will be developed to show how the other concentrations were determined.

From Section V of this report, the average methanol emissions from light and heavy duty vehicles in a typical tunnel would be 0.38 g/mile. Per the model developed by Southwest Research Institute (2), an average emission factor of 1 g/mile of any pollutant for traffic in a typical roadway tunnel would result in a concentration of 1.12 mg/m^3 for that pollutant. Multiplying this by the average emissions of 0.38 g/mile gives an expected methanol concentration of 0.43 mg/m^3.

The street canyon situations are simulated by examining the parameters of two street canyons. The typical condition is calculated for a four lane street canyon with a traffic load of 800 vehicles per hour and sidewalk location of the exposed population. The severe condition is based on a six lane street canyon with a 2400 vehicles per hour traffic load, and sidewalk location of the exposed population.

Three different cases were considered in order to cover the possible range of exposures in an expressway situation. The typical on road exposure is based on a four lane expressway with a traffic load of 1400 vehicles per hour and a wind of 1.0 meter/second at 315 degrees to the direction of travel. In this situation, the exposed population is located inside the vehicle. The severe case represents an identical situation except with much more traffic (3675 vehicles/hour), on a ten lane freeway. The third case necessary to consider is the "off road" case which is an exposure involving a close proximity to the highway (i.e., living or working close to it). This case is calculated on a short term basis (rush hour) for a distance of 100 meters downwind of the roadway.

Garages

The typical personal garage situation represents a 30 second vehicle warm-up time, and the severe situation simulates a five minute vehicle warm-up time. Both of these cases, of course, take place within a residential garage with the door open, and are intended to correspond to summer and winter conditions, respectively. Evaporative emissions, as well as idle emissions will be examined.

Currently, methanol idle emission data are only available from one vehicle - a VW Rabbit tested with various catalysts and calibrations. Methanol emissions at idle range from 0.001 to 0.034 g/min., averaging .007 g/min. However, these tests are with a warmed up engine and catalyst rather than cold-starts as would occur in a garage scenario. So, a more accurate assessment of cold-start idle emissions might come from using idle tests of this vehicle without a catalyst. These data range from 0.18 to 0.31 g/min., with an average of 0.24 g/min. In a personal garage under the severe exposure situation, 0.24 g/min would yield a methanol concentration of 16.08 mg/m^3.

Evaporative emissions in a personal garage are potentially a greater problem than start-up emissions, because the garage door would more likely be closed, reducing the ventilation from 615 cfm to 20 cfm. Only the hot soak situation will be examined, since these emissions are usually greater than the diurnal heat build emissions of methanol.

To calculate expected methanol concentrations from evaporative emissions, it will first be assumed that vehicles will meet the standard of 2.0 g HC/test. As described in Section V, this would result in one-hour hot soak methanol

emissions of 3.33 grams due to inclusion of the oxygen mass. In a typical residential garage of 2189 ft^3 (61.95 m^3) the resulting concentration of methanol, neglecting ventilation, would be 54 mg/m^3. With ventilation taken into account (20 cfm), the lower bound on the concentration would be 30 mg/m^3. This figure corresponds to an initial concentration of 54 mg/m^3 reduced over a one hour time period by ventilation at 20 cfm, with no further methanol evaporated during that hour. Since what actually occurs (continuous evaporation and continuous ventilation) is somewhere in between 54 mg/m^3 and 30 mg/m^3, the concentration corresponding to 3.3 grams of evaporated methanol is estimated to be 40 mg/m^3.

The exposure to this concentration of 40 mg/m^3 would occur only if a person re-enters the garage within the hour, and the exposure will also usually be short, lasting from the time the person enters the garage until either the ventilation from the opened garage door reduces the methanol concentration significantly or the person drives out of the garage. After 10 minutes with the garage door open the concentration in the garage would drop by 94% (3, Figure 21).

The typical parking garage case simulates an above the ground, naturally ventilated garage in which it is assumed that a vehicle spends an equal amount of time on both the

parking level and ramp level. The emission factors used in this scenario are idle emissions, since there are no data available for any parking garage driving cycle. The severe case represents an underground garage wherein the exposed population is assumed to be at the lowest parking level. It is also assumed that this exposure occurs 20 minutes after a major event in which the parking structure is emptying from an essentially full condition. The initial concentration of methanol is assumed to be low (1 ug/m^3), since the ventilation system in a parking garage would remove most of the evaporative emissions as they occur (2).

Concerning evaporative emissions in a parking garage, the only potentially high concentration situation would be following the arrival of many vehicles, which then proceed to give off hot soak emissions. This is not expected to be a problem for two reasons. First, there is plenty of ventilation (30,000-40,000 cfm per parking level compared to 20 cfm for a closed-door personal garage). Secondly, immediately after parking, the drivers would leave the garage.

Table III
Ambient Air Scenarios
Methanol Concentrations (mg/m^3)[a]

Scenario	Entire Fleet CH_3OH Fueled	Entire Fleet CH_3OH Fueled 25% Malfunction	25% of Fleet CH_3OH Fueled	25% of Fleet CH_3OH Fueled 25% Malfunction
Roadway Tunnel				
Typical	0.43	2.87	0.11	0.72
Severe	1.09	7.31	0.27	1.83
Expressway				
Typical	0.02	0.05	0.01	0.01
Severe	0.10	0.21	0.03	0.05
Close Proximity	0.02	0.04	0.01	0.01
Street Canyon				
Typical	0.06	0.13	0.02	0.03
Severe	0.41	0.88	0.10	0.22
Parking Garage				
Typical	0.03	0.94	0.01	0.23
Severe	0.39	3.63	0.10	0.91
Personal Garage[b]				
Typical	0.06	1.90	0.06	1.90
Severe	0.47	16.08	0.47	16.08
Hot Soak	40.00	40.00	40.00	40.00

[a]Based on weighted average emission factors from Table I.

[b]Since the personal garage scenario considers only one vehicle, the 25% malfunction and/or methanol-fueled fractions in columns 2, 3, and 4 were not taken.

Vehicle Refueling Exposures

With the use of methanol as a fuel, another scenario that needs to be investigated is the exposure encountered by a vehicle owner filling up his fuel tank at a self service station. According to 1982 information from EPA's FOSD it was found that 75% of the refueling is done on a self serve basis (42).

The estimate of methanol exposure presented here is a very rough estimate based on the limited exposure data that was collected for benzene (43). It was found that a person refueling a car with gasoline would be exposed to about 0.785 mg/m^3 of benzene from gasoline vapor containing 0.8% benzene. This means a total gasoline vapor exposure of about 100 mg/m^3. Since methanol has a vapor pressure approximately half that of gasoline, a typical refueling would result in a methanol concentration of about 50 mg/m^3. The average refueling time for a gasoline fueled automobile is 1.7 minutes. For methanol, with its lower energy content, average refueling time would double, to 3.4 minutes on the average.

VII. Methanol Health Effects

Ingestion Studies

A literature review concerning the health effects of methanol was performed by Midwest Research Institute (3). In addition to inhalation data, this review also covered exposures from ingestion and skin absorption, which could occur with use of methanol as a vehicle fuel.

Practically all the methanol toxicity data involve its ingestion with, or as a substitute for, ethanol (ethyl alcohol). The immediate symptom is an inebriation, indistinguishable from that from ethanol ingestion. After 12 to 18 hours, the characteristic methanol toxicity appears, presumably caused by its metabolites, formaldehyde and formic acid. Symptoms include headache, weakness, leg cramps, and vertigo; nausea and vomiting sometimes with violent abdominal pain; back and leg pain; vision defects; rapid, shallow breathing from metabolic acidosis; and weak, rapid pulse with hypotension; progressing to apathy and coma, or to excitement, mania, and convulsions. Death, if it occurs, is usually from respiratory failure. In nonfatal cases, convalescence is often protracted and complicated by debility, blindness, and kidney problems.

Relatively few experimental studies on methanol toxicity have been published, and most of them involved very large doses, mechanistic studies of the retinal toxicity, or both. Most human reports are case studies, with little exposure data. Toxicity has occurred from ingestion, inhalation, contact, and confounded exposure through two or all three routes.

Methanol's toxicity (especially its ocular effects) is generally believed to be caused by its metabolities, although its metabolism is not fully understood. In humans and other primates, methanol is first oxidized to formaldehyde by the enzyme catalase, but in lower animals this oxidation is effected by alcohol dehydrogenase. The highly reactive formaldehyde quickly disappears from the tissue and was formerly believed to be the cause of toxic effects. More recently, the further metabolites, formic acid or formate esters, have been suggested to be the toxic products (38).

Animal Studies

The bioassay data were limited in applicability to human toxicity, but did demonstrate that in the animal <u>in vitro</u> systems studied, methanol is not very toxic and not mutagenic. In the one in vitro respiratory tissue study, the exposure to 0.4 to 1.4 mg methanol in aerosol at the rate of 27 ml/sec for 2 seconds inhibited ciliary activity in the

esophageal tract of the leopard frog. Another study found low levels of methanol (15 ug) increased release of lung prostaglandins; higher methanol levels decreased rate of release (3).

In different animal studies the results varied quite a bit. Rats exposed to 50 mg/m^3 methanol for 12 hr/day for 8 weeks developed respiratory tract irritation, liver degeneration, and cortical neuropathy, but no such effects were found at 1.77 mg/m^3 (39). Similarly, minor toxicity was found in rats exposed continuously to 5.32 mg/m^3 methanol. Dogs exposed to about 600 mg/m^3 methanol 18 hr/day for over a year developed no noticeable adverse effects.

Human Studies

Human experimental studies have not been conducted specifically to identify methanol health effects by inhalation, but several studies have determined an odor threshold for methanol. The highest of these was 7,800 mg/m^3, while the lowest was 4.3 mg/m^3 (3).

Experiments have also been conducted measuring eye sensitivity to light(39). A threshold of 3.3 to 3.7 mg/m^3 was found for degradation of light sensitivity (dark adaptation), and 1.8 to 2.4 mg/m^3 had no effect. At a

concentration of approximately 4.5 mg/m^3 the pattern of dark adaptation was markedly altered from that of the controls.

One documented study of occupational exposures to methanol found that a group of office workers exposed to about 22 to 500 mg/m^3 from spirit duplicating machines experienced recurrent headaches. Workers who were actually operating the machines had more severe symptoms (3).

Skin Absorption

Various animal studies have shown methanol exposure via skin absorption to have effects similar to inhalation (3). Also, recent work with humans has shown methanol skin absorption and ingestion to result in similar quantities of methanol being excreted in urine and exhaled air indicating similar effects on the body.

VIII. Determination of the Range of Concern and Conclusions

The definition of "range of concern" is that range of exposure concentrations which may be detrimental to human health. The lower value of this range would be the lowest concentration at which there is some suggestion of adverse physiological effects. The upper value of this range would be that level above which the studies show that the pollutant causes so great a health risk as to strongly suggest it be avoided. The Threshold Limit Value* (TLV) for a given pollutant is usually appropriate to use as the upper level of the suggested range of concern.

Although it would be more appropriate to consider exposure concentrations relative to their corresponding exposure times for each resulting health effect, this degree of detail was not feasible with the data available. The determination of the range of concern was based primarily on acute human experimental studies, since these were thought to most closely simulate the exposure situations examined in this report.

*The Threshold Limit Value, set by the American Council of Governmental Industrial Hygienists, is the recommended maximum time weighted average concentration to which workers can be exposed for an 8-hour work day or 40-hour work week.

The Threshold Limit Value for methanol inhalation exposure is 260 mg/m^3, which is suggested as the upper limit of the range of concern. Although a direct comparison of inhalation vs. ingestion exposure would not be valid due to uncertainties in absorption and metabolism processes, it is interesting to note the correlation that seems to exist in the exposure range around the TLV.

One reference (40) indicates that the lowest ingested dose at which some toxic effect occurred for humans was 100 mg/kg body weight. For a 70 kg (154 lb) person this translates into 7 grams or 8.75 ml. Another study (4) cited one unusual case in which ingestion of only 3 teaspoons of 40% methanol (6 ml methanol) resulted in death, whereas a third study (41) reported no toxic reaction from ingestion of about 2 ml. For comparison, an inhalation exposure at the TLV of 260 mg/m^3 would yield an 8 hr. cumulative exposure of 3.25 ml if it were all absorbed (3). However, it is probably not valid to compare absorption and ingestion in this fashion.

Documentation of adverse physiological effects of low level methanol exposure is poor, making the selection of a lower limit to the range of concern difficult. The level suggested as the lower limit is 4.5 mg/m^3, which was the level at which the pattern of dark adaptation markedly altered from that of the unexposed control sample (39). These changes

resulted from a 5-minute exposure, but they were reversible within a couple hours following exposure.

Below this level certain physiological effects have been found, such as changes in the alpha-rhythm amplitude of the cerebral cortex reflex activity (1.17 - 1.46 mg/m^3). It is not known whether these alpha-rhythm changes represent adverse physiological effects or just altered physiological parameters. Since the limits of the range of concern are based on evidence of adverse physiological effects, 4.5 mg/m^3 is considered to be conservative (i.e. on the low side) for the lower limit of the range of concern.

The next step in making use of this suggested range of concern is to translate it into terms of automotive emission factors for each scenario. Table IV shows fleet average emission factors that would result in the lower and upper limits of the ambient air range of concern. Since these numbers are total emission factors, they include the evaporative emissions (for the street canyon scenario) as well as the tailpipe emissions.

Table IV

Emission Factors (g/mile) Corresponding to the Lower and Upper Limits of the Methanol Range of Concern

		4.5 mg/m^3	260 mg/m^3
Roadway Tunnel	(typical)	4.01	231.5
	(severe)	1.58	91.0
Street Canyon	(typical)	107.14	6190.5
	(severe)	15.96	922.0
Expressway	(typical)	36.88	2131.1
	(severe)	9.09	525.3
	(off road)	42.86	2476.2

Comparing these figures with the emissions listed in Table I, it appears that the severe tunnel scenario is the only one of the roadway scenarios having the potential for exposure within the range of concern. Using the weighted average emission factors from Table I, the average emission factor for each scenario can be compared to the corresponding lower limit of the range of concern. This is done in Table V.

Table V

Range of Concern Compared to Potential Emissions
grams/mile

	A	B	C
	Limits of Range of Concern (Severe Case)[a] i.e. Fleet Average Emissions Needed to be of concern	What Fleet Average Emissions Would Be Assuming 100% CH_3OH Fueled, Catalyst-equipped Vehicles[b]	Column B with 25% of Fleet Malfunctioning Severely[b]
Roadway Tunnel	1.58- 91.0	0.38	2.56
Street Canyon	15.96-922.0	1.44	3.12
Expressway	9.09-525.3	0.20	0.41

[a]From Table IV
[b]From Table I

As shown in Table V, even if it is assumed that all light and heavy duty vehicles on the road are methanol fueled (with oxidation or 3-way catalysts), the emissions could be within, but not above, the suggested range of concern for the severe roadway tunnel scenario. The street canyon and expressway scenarios appear to be below the suggested range of concern.

Garage scenarios were discussed in Section VI. Parking garage exposures, even with all vehicles using methanol, would be below the suggested range of concern, based on the few idle and evaporative tests that have been run. However,

personal garages are estimated to have as much as 16 mg/m^3 during a cold start, and as much as 40 mg methanol/m^3 during periods of hot soaks. Exposure to this concentration would probably be brief, but within the range of concern. Therefore, further monitoring of idle and evaporative emissions from methanol fueled cars may be appropriate, since exposures in this scenario are likely to occur much sooner than any of the roadway or parking garage scenarios which call for a large fraction of the vehicle fleet to be methanol fueled.

Vehicle refueling exposures, as discussed in Section VI, could involve concentrations of approximately 50 mg/m^3 for a few minutes at a time, each time the tank is filled. This is within, but not above, the range of concern, and therefore, may call for closer examination as to possible adverse effects and methods of minimizing this type of exposure. For instance, Stage II refueling loss controls would be one way of reducing these emissions and resulting exposures. Use of Stage II control may be easier here than for gasoline-fueled vehicles since both the vehicles and service station pumps would probably be newly designed.

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